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Vanadium removal from venezueian crude oil

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VANADIUM REMOVAL FROM VENEZUELAN CRUDE OIL

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CERTIFICATE OF APPROVAL

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ABSTRACT

An investigation was made to determine the feasibility of removing vanadium impurities from an asphaltic Venezuelan crude oil, by means of liquid extraction. A theoretically "reasonable" solvent, aqueous acetamide, as well as ethylene glycol monobutyl ether, a solvent with proven utility on nonasphaltic Middle Eastern crude oils, were tried without success. These results, when viewed in the light of work of previous investigators, tend to indicate that liquid extraction has a very limited potential in removing vanadium from asphaltic grades of crude oil.

INTRODUCTION

Vanadium in Crude Oil

The presence of vanadium in crude oils extracted from various parts of the world creates many problems for both the refiner and some ultimate users. To the refiner, it is a very effective catalyst poison in his cracking and hydrodesulfurization operations. Users burning heavier fractions (residual fuel oils, etc.) cut from crudes containing vanadium find that the element promotes rapid corrosion in equipment combustion chambers. These two problems alone cost many millions of dollars every year in material and equipment replacement.

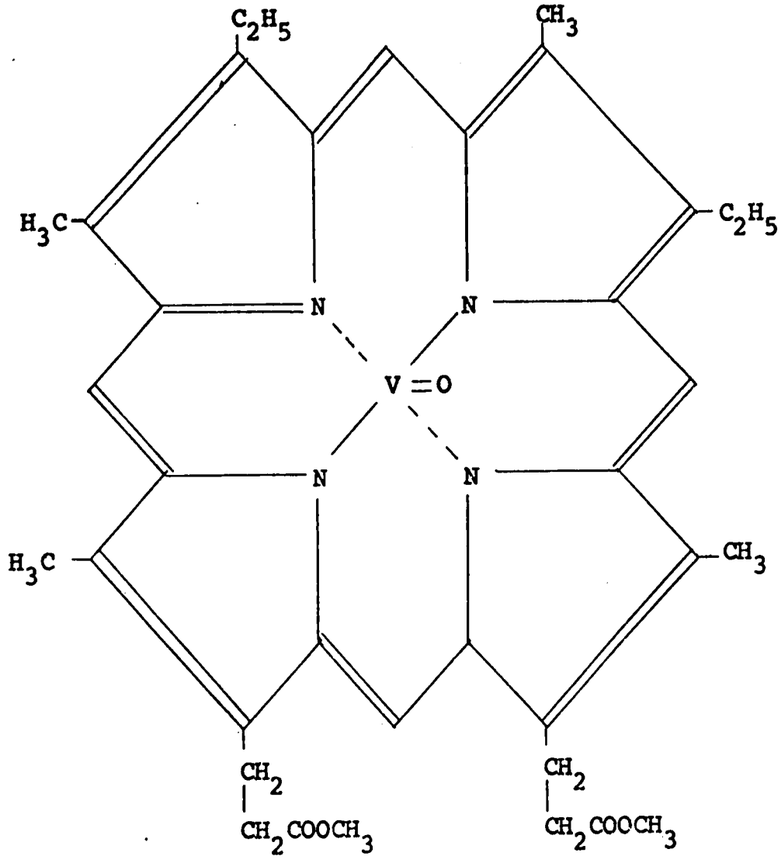
Venezuela currently produces around one billion barrels of crude oil every year, of which the United States, and primarily the Eastern Seaboard, gets about 55%. Crudes from Venezuela are some of the dirtiest in the world. Besides having very high vanadium concentrations (up to 1400 parts per million), they are also very high in other heavy metals (especially nickel), sulfur, and nitrogen. It has been estimated that from

Venezuela's annual crude oil production alone, there is enough vanadium to supply the world's annual requirements for the metal.[1] The metal is presently burned to various oxides during fuel combustion, swept through fly ash collectors and stacks with combustion product gases, and thus effectively lost for further use.

Molecular Form and Origin

The nature of the vanadium compounds in crude oil was studied as long ago as 1935.[2] At this time they were discovered to be a porphyrin complex. Today, it is widely agreed that there are two classes of vanadium compounds present in crude oils. Both classes are very stable, nonionic, oil soluble complexes which seem to have the same basic structure, but differ in the overall size of the molecules.

Type I compounds have been described as having the following structure:[3]



These molecules have molecular weights around 550, and are quite volatile, having boiling points around 1180°F. They are believed to be monomeric, planar molecules.

Type II compounds are believed to be very high molecular weight porphyrins. They are probably dimeric or polymeric molecules with large asphaltic side chains, probably held together through sulfur linkages. These molecules are nonvolatile.

Considerable thought has been given to the question of the origin of the vanadium in the crude oil. Type I compounds are seen to be very similar to the iron porphyrin complex, hematin, found in the blood of vertebrates. There is also a striking similarity between it and the chlorophyll found in plants. Vanadium is relatively common in all living matter, with the highest known concentrations in small sea animals called ascidians, which can have a vanadium percentage of 0.65, based on dry weight. Perhaps the most reasonable explanation of the origin would be that ancient flora and fauna of marine origin degraded primarily to compounds containing only hydrogen and carbon, with any residual metals remaining in certain stable molecular configurations which were compatible with the hydrocarbons.

Unconventional Separation Techniques

There have been numerous approaches to the problem

of removing vanadium from petroleum. In as much as it is a problem with obvious industrial interest, almost all available, documented research is in the form of domestic and foreign patents.

A method for changing the oxidation state of the vanadium in hydrocarbons has been patented.[5] In this operation, the oil is treated with an oxidizing agent capable of liberating the metal from its complex. Once this is done, the resulting insoluble inorganic oxide may be separated by any of a number of customary mass transfer operations. A recommended procedure is to heat the oil carrying vanadium with chromium trioxide for 6½ hours at 106°C, under total reflux. While the method is effective, it would appear to be a fairly high energy consumer when Venezuela's total annual crude oil production is considered.

A thermal diffusion process has been proposed.[6] This involves feeding the petroleum into a thermal diffusion chamber having a dual wall temperature gradient in the neighborhood of 200°F. This process is stated to be rather slow.

A third method utilizes a countercurrent extraction column, operated around 600°F, where a molten sodium-lead

alloy is contacted with the petroleum containing vanadium.[7] Although the vanadium can be effectively removed from the oil, the oil picks up sodium sulfide, which must then be removed through an electrical desalting apparatus. A special electrolytic cell for rejuvenating the alloy is also an inherent part of the process. The operation appears to be a fair consumer of electrical energy.

A French process treats a petroleum sample containing vanadium with a complex solution of aluminum, magnesium, and ammonium chlorides and acetates.[11] The vanadium porphyrin compounds are said to separate from the petroleum and form an emulsion between the aqueous and organic layers. No process efficiency or petroleum losses are mentioned in this patent, and the reason for this phenomenon taking place is quite obscure.

The scientific curiosities described above are not the only methods which have been considered. Some of a more reasonable nature are described next.

More Realistic Approaches to the Problem

A proposal has been made to solvent treat a vacuum

distillation residue, thermally crack the resultant insoluble residue, then gasify the coke remaining from the cracking operation.[8] In this process an upgraded extract is obtained from the solvent treatment step, and from the cracking and gasification step an inorganic residue and a low calorific value gas is obtained. The sensible heat from gasification is used to carry out the thermal cracking. The method appears to be feasible, but would have a tremendous energy loss.

Another approach involves a liquid extraction process which includes a chemical reaction. This method mixes a petroleum product or crude oil containing vanadium with a liquid alkyl sulfonic acid.[9] Contact times are stated to be 30 minutes, and temperatures can be 10 to 250°C. The system is a 2 phase one, with the acid layer picking up porphyrin complexes and heavy metal salts. Multiple extractions are frequently required. Although a reasonable vanadium separation is brought about, crude oil losses of 35% were observed after only 2 batch extractions. The process takes advantage of a commonly used laboratory technique in which sulfonic acids are added to petroleum samples to be ashed prior to final analysis for heavy metals. The sulfonic acids

effectively breakdown the porphyrin molecules and thus prevent their escape through volatilization.

Several liquid extraction techniques have been tried. A process for treating distillates containing heavy metals has been patented.[10] A 2-pyrrolidone-alcohol mixture is said to be immiscible with moderately boiling hydrocarbon fractions, while at the same time being an excellent solvent for metalloporphyrin complexes. Separations are said to be brought about through any conventional liquid extraction scheme. The process is quite efficient if only the volatile Type I molecules are present, but it cannot remove the larger Type II molecules from a hydrocarbon solution. Its use is therefore limited.

A very interesting process involves classical liquid extraction techniques using ethylene glycol monobutyl ether (EGMBE) as the solvent.[12] The process is somewhat different than techniques discussed previously, in that the EGMBE is supposed to extract the main part of the hydrocarbon, without dissolving the metallic impurities. The solvent is said to concentrate sulfur, nitrogen, and nickel is a very small fraction of the crude. When EGMBE is added to the crude oil, 2 liquid

phases are said to form immediately: the lighter phase containing the demetallized crude, and the heavier phase containing some asphaltenes and all mineral impurities. Greatly varying contact temperatures and solvent to oil ratios are said to work well, and, of course, most any apparatus available can be used to carry out the process. A Middle Eastern crude oil processed with this solvent lost 20% of its original weight, but was very effectively demineralized.

A process utilizing a liquid extraction separation to bring about the removal of vanadium compounds following moderate hydrotreating of the petroleum has also been patented.[13] The hydrotreating is said to convert Type II molecules to Type I molecules by breaking the suspected sulfur linkages which attach the asphaltic groups to the porphyrin bases. The hydrotreating conditions recommended are said to be mild enough so as not to cause degradation of the porphyrin molecules themselves. Considerable pressures (200 to 2000 psi) and fairly high temperatures (600 to 950^{o}F) are required nevertheless. Once the hydrotreating has been accomplished, heavy metals are said to be removed fairly easily with any of a number of extraction solvents. The hydrotreating catalyst used can even be V_2O_5, obtained from the feed itself.

Petroleum Extraction Solvents

The processes mentioned above seem to indicate that liquid extraction would be the most economical means of bringing about the separation of vanadium compounds from crude oil, if a suitable solvent could be found.

In an attempt to find a suitable solvent, a study was made of commercial extraction systems utilized in the petroleum industry. The first system noted uses 2-pyrrolidone to remove aromatic materials from a stream of paraffinic hydrocarbons.[14] 2-pyrrolidone is said to effectively remove ben zene, substituted benzene compounds, toluene, xylene, etc., as well as polynuclear aromatic hydrocarbons. It has already been mentioned that this solvent can be used to remove Type I vanadium compounds from petroleum distillates.

N-acyl pyrrolidones have been used in a similar process for removing liquid unsaturated hydrocarbons from liquid saturated hydrocarbon streams.[15]

A much more recent process, called the Formex process, uses N-formylmorpholine (FM) to extract benzene, xylene, toluene, etc. from feedstocks.[16] FM is a dieterocyclic amide. This process, utilizing the novel

solvent, is said to at least equal the efficiency of presently used solvents, and yet be more flexible in handling feedstreams of greatly varying compositions.

Investigation

Because of the inherent advantages of a liquid extraction system, an experimental program in this area was planned to further investigate the problem. By observing previously used techniques and solvents, it was quite evident that all the solvents are organic compounds which are fairly polar. Quite obviously they were an attempt to capitalize on the porphyrin molecules vanadyl-nitrogen polarization in order to pull it from the hydrocarbon matrix. If the solvent-vanadium molecule attraction theory is valid, the use of a more polar molecule could possibly enhance the separation. With an eye on the FORMEX process, it was considered worthwhile to evaluate the effectiveness of an amide as an extraction solvent.

Thus an experimental program was planned using an aqueous acetamide solution as a solvent. Acetamide was selected for various reasons. It is a fairly inexpensive, very polar organic compound. It has also been used to increase the water solubility of essentially

insoluble materials through various reaction mechanisms. Aqueous pyrridine solutions have been used to remove vanadium compounds from crude oil,[17] so the presence of water in the solvent was believed to do little harm, and it was hoped that it would help keep an insoluble liquid phase in the extraction system.

To evaluate its effectiveness, the results of the aqueous acetamide extractions would be compared to the results on the same crude oil using EGMBE, the most promising and effective solvent discussed in the literature.

EXPERIMENTAL PROCEDURE

Extraction Procedures

All extractions were carried out in a controlled temperature Eberbach Water Bath Shaker. For the aqueous acetamide solutions, 250 mL Erlenmeyer flasks were used. Since only 50 ml. systems were run, the thin layers with relatively large surface areas were felt to enhance mass transfer.

Various vessel loadings were used. Initial runs with aqueous acetamide were made by first weighing the crude oil into a flask, and then pouring the solution over it. Other runs were loaded by mixing the acetamide with the crude oil, leaving the system overnight for approximately 14 hours, and then pipetting water into it. In as much as no advantage could be seen with either method, subsequent runs were loaded in the manner described first.

Extraction times were quite arbitrary. Initial work was planned to obtain rate of transfer data, but, since the process appeared to be so slow, the following experiments used contact times of 6 hours. This time was believed to set a reasonable limit on the process.

Phase separations for this system were carried out in a separatory funnel. In the water bath, an emulsion formed quickly, but in all cases it broke in the funnel after 2 hours or so. The phases proved essentially insoluble, and were readily separated.

200 ml. pyrex centrifuge flasks were used for the extractions with ethylene glycol monobutyl ether. Contrary to the patent's physical description, EGMBE did not form a two liquid phase system with the Venezuelan crude oil used in this investigation. When a sufficient volume of solvent had been added to the oil, a brown precipitate formed, which proved to be quite resistant to separation.

Three methods were tried in attempts to remove this solid phase from the liquid. Vacuum filtration caused a tarry mass to clog all available grades of filter paper and sintered glass crucibles. Next, centrifuging was attempted. Although this very effectively removed the precipitate, leaving a relatively clear but dark extract, following additions of solvent were unable to break up the tar deposited on the bottom of the centrifuge flask. This situation was not felt to be conducive for good interphase mass transfer. Gravity settlement in the

centrifuge flask, over a three day period, followed by decanting, proved to be the most satisfactory method of phase separation. The solids obtained in this way were quite fluid, and mixed easily with following batches of solvent.

Chemical Analysis

Crude oil, extracts, and raffinates were analyzed for total vanadium present. No attempt was made to determine the relative amounts of Type I and Type II compounds.

Samples were first ashed in the company of benzene sulfonic acid,[18] a chemical which decomposes any porphyrin compounds present, and thus prevents their loss through volatilization. The resulting ash was dissolved in electronic grade hydrochloric acid. The best method for completing the analysis was found to be direct analysis of the acid solutions on an atomic absorption spectrophotometer.[19] A Jarrell-Ash Model 802 Dial Atom, using a J-A #45453 bulb was used for this purpose. Calibration standards were prepared from vanadium pentoxide dissolved in the same hydrochloric acid. Analyses of both the hydrochloric acid and the benzene sulfonic acid showed no

traces of vanadium.

Materials used in this investigation are listed in Table 10.

RESULTS

Aqueous Acetamide Extractions

Initial work with this solvent mixture was planned in order to determine the optimum contact times for the extraction process. The results of the initial series of runs are shown in Table 1. The loading procedure used was to pour the aqueous solution into a flask containing the crude oil. Convenient values of temperature, water-acetamide ratio, and the amount of crude oil used were selected.

Table 2 shows the results of a similar series of runs obtained by changing the mixing method. The acetamide was first mixed into the oil, with water added 14 hours later. Again the temperatures and concentrations were arbitrarily selected.

Nearly saturated acetamide solutions were used as solvents, since lesser concentrations showed no results. Table 3 is a listing of the solutions used in the next series of runs. Results for this series are given in Table 4. Some vaporization of the crude occurred during the 55°C run.

Aqueous acetamide solutions obviously have no utility in removing the vanadium compounds from the crude

oil, so no further work was planned with this solvent.

Ethylene Glycol Monobutyl Ether Extractions

An experimental program with EGMBE was planned to determine its effectiveness on the asphaltic Venezuelan crude oil, since the "patent" crude was a Middle Eastern one. It was immediately apparent that the solvent is unable to form a two liquid phase system with LaRosa 533Tk. Approximately 15 grams of crude oil was used as a starting point to which continuous additions of EGMBE were made. Observations during this procedure are given in Table 5. As can be seen, the system does not form two liquid phases.

To determine quantitatively the amount of vanadium able to be removed from the crude oil with this process, a multiple extraction procedure was carried out. The solutions were mixed at a constant temperature for 1½ hours, the phases were separated, and fresh solvent was added to the raffinates created. Results for this operation are given in Tables 6 and 7. It is obvious that the solvent has no preferential removal capability, but merely progressively dissolves the crude oil.

Once this stage in the investigation was reached, the decision was made to abandon further liquid extraction trials.

Crude Oil Analyses

The original crude oil was found to contain approximately 225 parts per million (ppm) of vanadium. Table 8 shows the results of a number of analyses made on LaRosa 533Tk.

A typical atomic absorption calibration curve is included as Figure 1. Table 9 gives the calibration data, along with some machine adjustments found to give optimum vanadium sensitivity on the Jarrell-Ash Dial Atom.

DISCUSSION

The two different mixing techniques used with aqueous acetamide were attempts to ascertain whether the vanadium transfer was diffusion or chemical reaction controlled. By adding crude oil to the flask first, and then the aqueous solution, a phase reversal would take place due to specific gravity differences. This procedure was believed to promote a diffusion mechanism, if one was present. To enhance a chemical reaction between the vanadium compounds and the acetamide, the acetamide was mixed with the crude oil, and after 14 hours of contact time, water was added to the mixture. The water quickly and effectively washed the acetamide out of the oil, but no vanadium carry over was found. The results of both mixing schemes were essentially the same: an emulsion formed immediately after placing the system in the water bath. Evidently mixing schemes have no effect on the process.

Contact times were set at 6 hours after rate studies proved inconclusive. Since no removal of vanadium was detected for contact times less than this, and times greater seem quite impractical, 6 hours was thought to be a reasonable choice.

Nearly saturated solutions of acetamide and water were used as extractants when the lesser concentrations proved incapable of bringing about a separation. These solutions, with the 6 hour contact times, were run to give an overall evaluation of the solvent potential. The negative results obtained indicated it had none. At this time, further work with this solvent was cancelled.

Initially it was not clear as to whether time or EGMBE concentration caused the appearance of the brown precipitate previously mentioned. At the completion of the evaluation, it was apparent that concentration was the cause, but nevertheless contact times of 1½ hours were used throughout the investigation. The precipitate formation was very strong evidence to support a conclusion that crude oils from different localities can have very different matrices. The solvent could be seen to progressively dissolve the entire crude oil fraction, with substantial vanadium being present in both phases. This fact indicated that EGMBE has no worth in extracting vanadium from LaRosa 533Tk, even though it may work very well on Middle Eastern crude oils.

The analyses of LaRosa 533Tk obtained from the

analytical procedure used appear to agree very well with published values.[20] This is especially encouraging when the manufacturer states that the Dial-Atom machine has approximately a 5% error at vanadium concentrations of 100 ppm.

Some information concerning the character of the crude oil would appear to be in order. As a result of a request the boiling point curve shown as Figure 2 was provided by Humble Oil. It is apparent that LaRosa is a very asphaltic crude oil.

Previous liquid extraction operations which proved successful appear to work only on distillate fractions or light Middle Eastern crude oils. Vanadium molecules present in these hydrocarbons are quite obviously the Type I compounds, of relatively small molecular weight. These molecules are accessible to solvent action, and thus can be removed relatively easily. The LaRosa 533Tk is a heavy asphaltic crude oil. The vanadium present in it is nonvolatile, a fact substantiated when an analysis was made leaving out the benzene sulfonic acid. Thus it is safe to say that the vanadium is tied up in large asphaltic groups, which effectively shield the vanadyl area from foreign solvents. It is certainly doubtful that a solvent could be found that would preferentially

separate carbon-hydrogen asphalt from asphalt containing vanadium.

CONCLUSIONS

Conclusions drawn from this work can be summarized by stating that liquid extraction, and possibly all other classical mass transfer operations, have very limited potential in separating vanadium compounds from asphaltic crude oils.

TABLE 1

EXTRACTION RESULTS AT 27°C
WITH 33.3% ACETAMIDE SOLUTIONS

Sample	Contact Time	Ppm V in Extract
1	15 min	0.
2	30 min	0.
3	1 hr	0.
4	2 hr	0.
5	6 hr	0.

Weight of Solvent: 25.0 gms

Weight of Crude Oil: 31.5 gms

TABLE 2

EXTRACTION RESULTS AT 25.5°C
WITH 40% ACETAMIDE SOLUTIONS

Sample	Contact Time	Ppm V in Extract
1	30 min	0.
2	1½ hr	0.
3	3½ hr	0.
4	5½ hr	0.

Weight of Acetamide: 10.0 gms

Weight of Crude Oil: 25.0 gms

TABLE 3

NEARLY SATURATED ACETAMIDE SOLUTIONS

Temperature, °C	Ml H_2O	Wt Acetamide	% Acetamide Solution
25.5	5.0	12.10	70.8
35.0	5.0	15.14	75.3
45.0	5.0	20.31	80.4
55.0	5.0	31.16	86.4

TABLE 4

EXTRACTION RESULTS WITH
NEARLY SATURATED ACETAMIDE SOLUTIONS

Temperature, °C	Gms Crude Oil	Gms Solvent	Ppm V in Extract
25.5	17.10	17.10	0.
35.0	20.14	20.14	0.
45.0	25.31	25.31	0.
55.0	36.26	36.16	0.

TABLE 5

PHASE OBSERVATIONS FROM MIXING LaROSA 533Tk AND ETHYLENE GLYCOL MONOBUTYL ETHER

Gms EGMBE	% Solution	Observations
7.44	32.9	One phase
12.69	45.6	
17.97	54.3	Appearance of fine particulate
27.19	64.3	
31.47	67.5	Heavier precipitation
39.57	72.3	Flask adherence of particulate
56.67	78.9	
75.16	83.2	

Weight of crude oil: 15.13 gms

System temperature: 27°C

TABLE 6

MULTIPLE EXTRACTIONS AT 24.5°C WITH EGMBE

Extraction No. 1

Sample	Gms Crude	Gms EGMBE	Gms Extract No. 1
1	15.09	7.32	1 phase
2	15.18	14.45	1 phase
3	15.19	32.53	39.75
4	15.25	57.07	70.32

Extraction No. 2

Sample	Gms Raffinate No. 1	Gms EGMBE	Gms Extract No. 2
3	7.97	29.59	33.57
4	2.00	57.95	58.44

Extraction No. 3

Sample	Gms Raffinate No. 2	Gms EGMBE	Gms Extract No. 3
3	3.97	29.75	30.48
4	1.51	57.57	57.49*

*EGMBE entrainment present

TABLE 7

PHASE WEIGHTS AND VANADIUM CONTENTS
OF MULTIPLE EXTRACTIONS WITH EGMBE

Sample No. 3

Extraction No.	Gms Raffinate	μ grams V in Extract
1	7.97	1709
2	3.99	565
3	3.26	72
		2346 Total

Sample No. 4

Extraction No.	Gms Raffinate	μ grams V in Extract
1	2.0	3476
2	1.5	315
3	-	138
		3929 Total

Total μ grams V in original oil sample:

#3: 3924 μ grams

#4: 3944 μ grams

TABLE 8

CRUDE OIL ANALYSIS DATA

Sample	Gms Crude	Ml HCl	Soln ppm	Ppm V in Crude
29-1	3.37	10.0	87	225
30-1	2.38	10.0	63	230
30-2	2.30	10.0	59	222
31-1	3.25	10.0	84	224
31-2	2.96	10.0	78	228

TABLE 9

TYPICAL ATOMIC ABSORPTION SPECTROPHOTOMETER
CALIBRATION DATA FOR ACIDIC VANADIUM SOLUTIONS

Ppm V	% A	Absorbance
0.	0.	0.
18.	4.7	0.0200
36.	9.0	0.0410
54.	12.75	0.0593
90.	20.5	0.0996
127.	27.0	0.1367
181.	36.5	0.1972
272.	49.0	0.2924

Optimum Machine Settings for Dial-Atom Machine

Bulb Current: 7mA
Gain: 6+
Oxidant (N_2O) flow: 20+ SCFH
Fuel (C_2H_2) flow: 17 SCFH
Tank feed pressures:
N_2O: 35 psi
C_2H_2: 15 psi

Best sensitivity was found to be near 20% A for a 100 ppm solution.

TABLE 10

MATERIALS USED IN THE PROJECT

Material	Source	Grade	Purity,%
Crude Oil	Humble Oil and Refining Co.	LaRosa 533Tk	--
HCl	Target Chemical Co.	Electronic	99.95
V_2O_5	Fisher	Certified	99.95
Acetamide	Fisher	Certified	99.9
EGMBE	Fisher	Purified	--
Benzene Sulfonic Acid	Eastman Kodak	Highest Purity	99.9

FIGURE 1

TYPICAL ATOMIC ABSORPTION SPECTROPHOTOMETER
CALIBRATION CURVE FOR ACIDIC VANADIUM SOLUTIONS

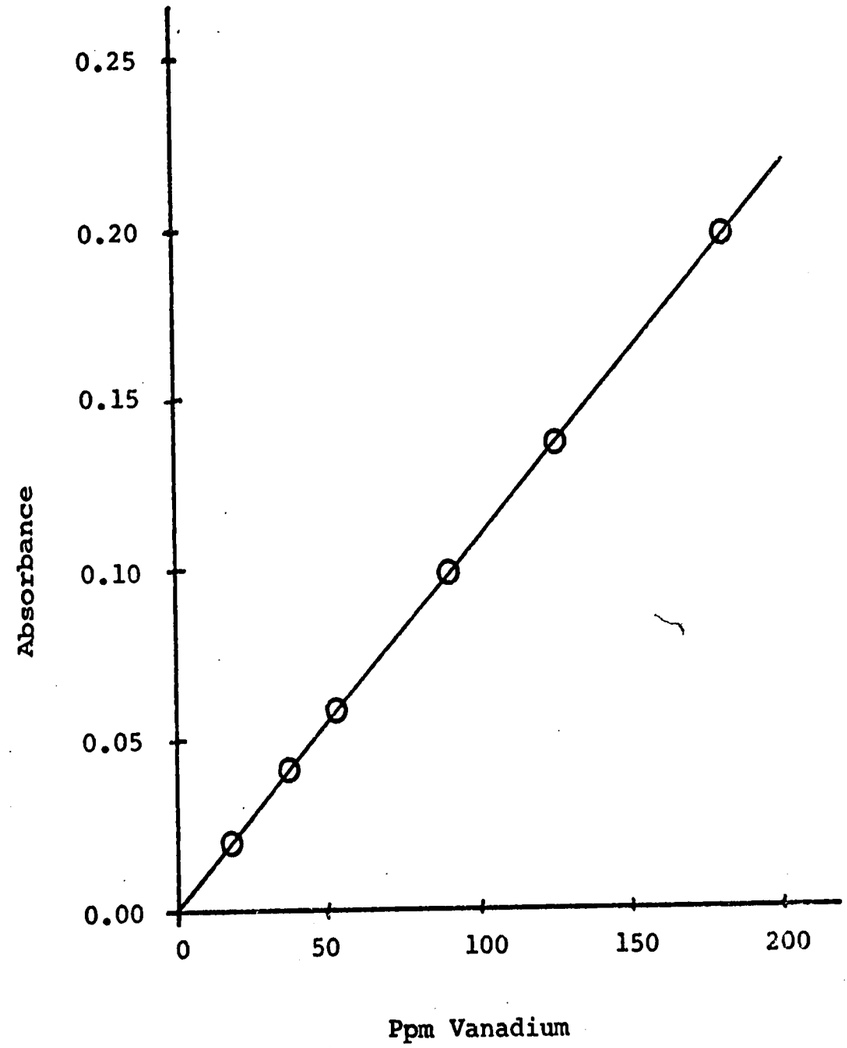
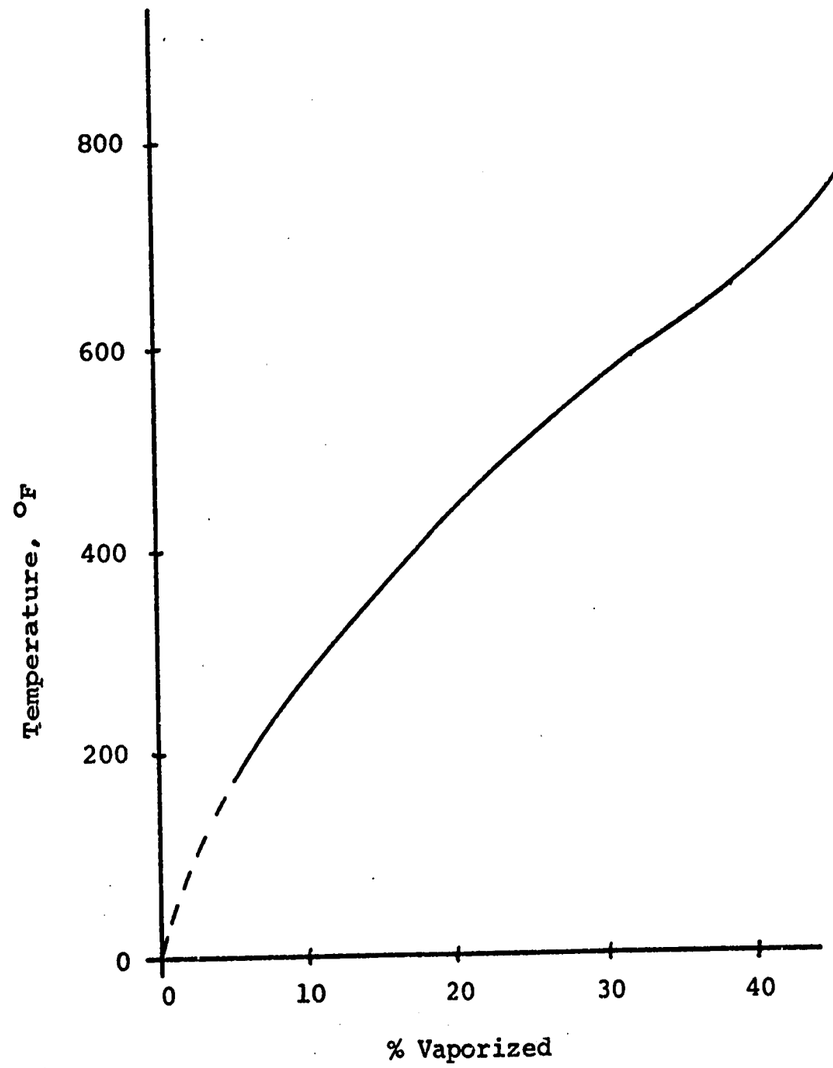


FIGURE 2

DISTILLATION CURVE FOR A TYPICAL LAROSA CRUDE OIL



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VITA

John E. Dumelow was born in Westerly, Rhode Island on June 4, 1945, the son of Mr. and Mrs. Lewis S. Dumelow. After attending public elementary and high schools in Westerly, he entered the University of Rhode Island. He was admitted to Tau Beta Pi and Phi Kappa Phi in 1966. In June, 1968, he received a Bachelor of Science degree in Chemical Engineering, as well as an R. O. T. C. commission in the U. S. Army Corps of Engineers.

Following two years of distinguished military service, most of which occurred in the Far East, he was employed by Hercules, Incorporated. In September, 1971, resigning from Hercules, he entered the Graduate School at Lehigh University to study in the Department of Chemical Engineering.

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